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Physical properties of calcium fluoride nanopowder after irradiation by relativistic electrons

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Abstract. Mesoporous CaF₂ nanopowders with specific surface area up to 91.5 m²/g have been obtained through evaporation by electron beam in vacuum. The effect of relativistic e-beam irradiation in air on magnetic and texture properties of CaF₂ nanoparticles has been studied. The influence of annealing and irradiation on the specific surface area and magnetization of CaF₂ nanopowder has been discovered for the first time.

1. Introduction

The physical properties of nanoparticles depend on numerous factors, namely, chemical composition, type of crystal lattice and degree of its imperfection, morphology, interaction of particles with the lattice and neighboring particles, phase composition and type of structure defects [1]. An efficient mechanism of action on nanostructures is irradiation by accelerated electrons, which changes the size of nanoparticles and, consequently, the particle properties. For example, the irradiation of ZnO nanoparticles by 6-MeV electrons decreased the particle size from 46 down to 15 nm [2].

The objective of this paper is to study the change in the properties of CaF₂ nanopowders (NPs) upon irradiation by a nanosecond relativistic e-beam at an URT-1M repetitively pulsed amplifier [3].

2. Experimental

The CaF₂ nanopowders were obtained by the method of evaporation by a pulsed electron beam in vacuum [4]. The technology of nanopowder generation, the applied methods of powder diagnostics, and properties of nanopowders are described in another our paper [5]. This paper reports the texture and magnetic properties of nanopowder upon irradiation.

Before irradiation, CaF₂ nanopowders were annealed in alundum crucibles at a temperature of 200, 400, and 900°C for 10 min. From here on, NP specimens before and after annealing are designated as S0, S200, S400, and S900, respectively.

The specimens were irradiated at the electron energy of 700 keV, the pulse duration of ~100 ns, and the pulse repetition frequency of 35 Hz. The time of irradiation was 15 min and then extra 15 min in a half of the specimens. The absorbed doses (AD) on the specimen surface were 31.5 and 63 MGy, respectively. The distance from an outlet to the irradiated objects was 5 cm. The nanopowder specimens were placed in aluminum foil pouches (foil thickness of 30 μm, thickness of the NP layer no larger than 0.5 mm), which were fixed on a massive aluminum plate cooled by fans. The



temperature of the aluminum plate was measured by a thermocouple. The temperature during irradiation did not exceed 70°C.

3. Results and discussion

The texture analysis (table 1) has shown that the adsorption/desorption isotherms of S0, S200, S400 specimens correspond to the IV type of isotherms according to the IUPAC classification, which is indicative of the mesoporous type of nanopowders. A significant increase in the specific surface (SS) of nonirradiated CaF_2 nanopowders after annealing at a temperature of 200°C was discovered (table 1). At the further increase of the annealing temperature up to 400°C, the specific surface decreased, and the annealing at 900°C has led to a sharp growth of the particle size and to the loss of mesoporosity in the S900 specimen.

Table 1. Texture properties of CaF_2 NP specimens at different absorbed doses (AD).

Specimen	S_{BET} (m^2/g)			$V_{\text{p-Total}}$ (cm^3/g)			D_{BJH} (nm)		
	AD, MGy			AD, MGy			AD, MGy		
	0	31.5	63	0	31.5	63	0	31.5	63
S0	64,3	79,8	91,49	0,25	0,519	0,46	21	27,9	25,2
S200	88,7	77,1	45,92	0,66	0,51	0,35	29	27,2	28,5
S400	52,4	70,02	79,25	0,30	0,51	0,46	22,5	26,3	26,3
S900	1,11	-	2,22	0,0025		0,0039	37	-	35,2

Here, $V_{\text{p-Total}}$ is the total pore volume, D_{BJH} is the mean pore diameter, S_{BET} is the specific surface area.

The irradiation of nanopowders leads to a marked increase in specific surface of CaF_2 nanopowders (table 1). For the S400 specimen, this increase was more than 1.5 times. All the nanopowder specimens, including those annealed at different temperatures, demonstrate the similar behavior: the specific surface increases with an increase in the absorbed dose of radiation. It should be noted that the smallest specific surfaces were characteristic of the specimens annealed at the lower temperature and the smallest absorbed dose. The absolute maximum of the specific surface was observed in the nonannealed S0 specimen at the maximal absorbed dose. This dependence breaks only for the S200 specimen irradiated by a dose of 63 MGy. This anomaly calls for the further study. The twofold increase of the specific surface and the 1.5-times increase of the total pore volume for the S900 specimen, which is no longer nano-sized, are surprising.

The irradiation of nanopowders surprisingly affects the total pore volume and the mean pore diameter. These parameters not only increase proportionally to the absorbed dose, but become practically uniform, especially, at a dose of 31.5 MGy, even for the S200 specimen (table 1). Thus, the irradiation by an electron beam allows us to control the change of texture properties of the specimens.

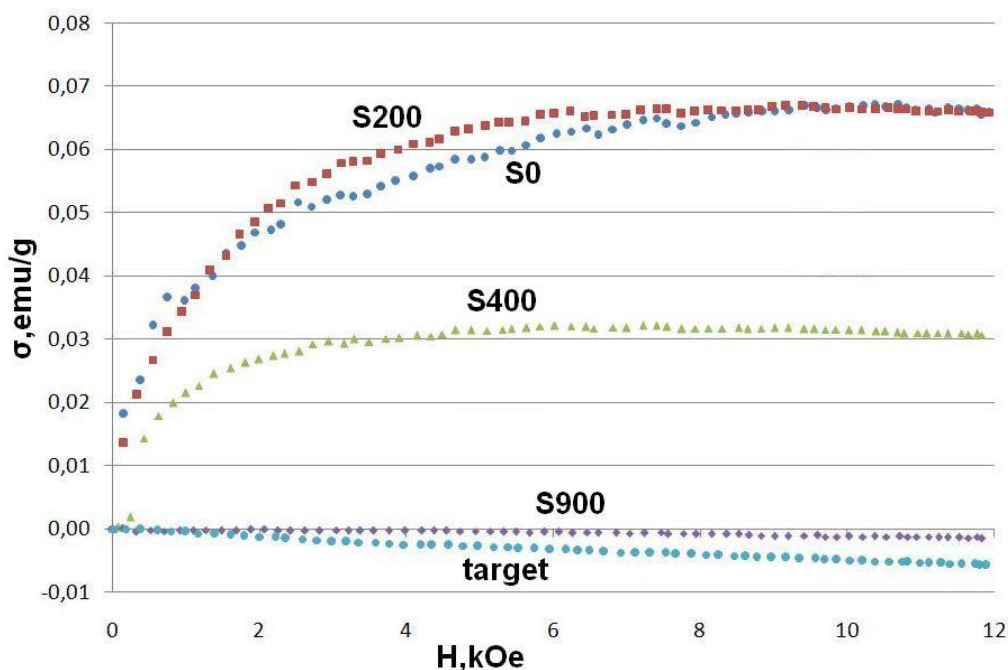
The data of EDX analysis given in [5] are indicative of the absence of any magnetic admixtures (Fe, Co, and Ni) in the S0 and S200 specimens and the presence of strong stoichiometry in the specimens, namely, the presence of excess calcium. It is also shown there for the first time that the nanopowders demonstrated the ferromagnetic (FM) behavior. This behavior can be explained by formation of structure and radiation defects characteristic of the used method of nanopowder generation [4]. It is assumed, by analogy with the model [6], that just fluoride vacancies take part in formation of the ferromagnetic response in the S0 and S200 specimens.

The measured magnetic properties of the nanopowders are shown in figure 1. Table 2 gives the values of magnetization measured at the magnetic field strength of 8 kOe. It can be seen from figure 1 and table 2 that the irradiation increases significantly the magnetization of CaF_2 nanopowders. The nanopowder specimens annealed at different temperatures prior to irradiation demonstrate the increase in magnetization for S200, then its decrease for S400, and nearly vanishing for S900.

Table 2. Magnetization of CaF_2 nanopowder specimens at different absorbed doses.

Specimen	Magnetization, emu/G at 8kOe		
	AD, MGy		
	0	31.5	63
S0	0,045	0,065	0,13
S200	0,06	0,065	0,05
S400	0,038	0,032	0,047
S900	0,005	-	0,033

The magnetic response of irradiated nanopowders is more complex. The S0 specimen shows a considerable increase in magnetization (more than 2.5 times at 63MGy) proportionally to the absorbed dose. The S200 and S400 specimens demonstrate some variations of magnetization upon irradiation, and these variations have the opposing signs. At the same time, the anomalous behavior is observed for the S200 specimen irradiated with the absorbed dose of 63 MGy, as in the case with the specific surface. The restoration and sharp increase (6.6 times) in magnetization of the S900 specimen irradiated with the dose of 63MGy became extremely surprising for us, especially, with allowance made for the fact that the irradiation with the smaller dose resulted in the loss of magnetization.

**Figure 1.** Magnetization curves of a target and CaF_2 specimens upon irradiation with the dose of 31.5 MGy.

Thus, for CaF_2 nanopowders generated by the method of evaporation by a pulsed electron beam, we can speak about the presence of correlation between the specific surface and magnetization. This correlation manifests itself at different impacts, such as thermal annealing and irradiation by relativistic electrons.

The variations of the specific surface and magnetization of CaF_2 nanopowders under these impacts can be caused by the following factors: water evaporation from nanopowder mesopores, desorption of admixtures (calcium carbonate and hydroxide) from the surface of nanoparticles, oxidation of metal

calcium nanoparticles, and variation of the concentration and degree of clustering of dye centers under the effect of heating and irradiation. The influence of radiation and thermal annealing of surface defects on magnetization is obvious. The vanishing of the ferromagnetic response in the S0 specimen (0.045 emu/g) after annealing at the temperature of 900°C is connected with variation of the phase composition and morphology of the S900 specimen (oxidation of metal calcium nanoparticles can lead to formation of CaO oxide shells on the surface of fluoride nanoparticles). The re-appearance of the ferromagnetic response (0.033 emu/g) in the S900 specimen upon irradiation by relativistic electrons, which exceeded magnetization of the nonirradiated S900 specimen (0.005 emu/g) by an order of magnitude, unambiguously confirms that just e-beam irradiation is a cause for appearance of the ferromagnetic response in CaF₂ nanoparticles.

4. Conclusions

Thus, the change in the specific surface and magnetization of nanopowders at the prior annealing can be associated with the loss of substances adsorbed on the surface and in nanopowder mesopores and the change of their phase composition. It is possible that the intensification of the ferromagnetic response in CaF₂ nanopowders upon annealing in an oxygen-containing environment follows the mechanism similar to those described in [7] with participation of oxygen vacancies (fluoride vacancies in our case), which calls for additional study.

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